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Separation of ternary mixtures by pseudo-simulated moving bed chromatography

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Abstract

Modeling and simulation are presented of the separation of a ternary mixture by pseudo-simulated moving bed chromatography, according to the JO process of Japan Organo Co. The process cycle is divided into two steps. In step 1, feed and eluent streams are introduced into the system, equivalent to a series of preparative chromatographic columns, and the intermediate component is produced. In step 2, similar to a simulated moving bed (SMB), there is no feed and the less adsorbed species is collected in the raffinate while the more retained species is collected in the extract; this step is described by an equivalent TMB model. A parametric study is presented in order to analyze the sensitivity of the model to variations on the duration of step 1 and step 2 and on the intraparticle mass transfer coefficient. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Simulated moving bed chromatography; Pseudo-simulated moving bed; Ternary mixtures; Preparative chromatography

1. Introduction

Simulated moving bed (SMB) is one of the most powerful and promising techniques for preparative and industrial scale chromatography. In particular, the SMB technology allows the continuous injection and separation of binary mixtures. The simulated countercurrent contact between the solid and liquid phases maximizes the mass-transfer driving force, leading to a significant reduction in mobile and stationary phase consumption when compared with elution chromatography [1,2]. In the simulated moving bed systems the solid phase is fixed and the positions of the inlet and outlet streams are shifted one column in a synchronous way in the same direction as the liquid phase. The shifting occurs at every switching time, t^*; after a certain number of cycles, until a cyclic steady state is reached.

Since the first patent on SMB from UOP [3], several industrial SMB units were built with applications in different areas, such as the Parex process for the separation of *p*-xylene from C_8 mixture and the separation of olefins from paraffins [4] in the petroleum refining and petrochemicals industry; the citric acid purification and the Sarex process for the production of high fructose corn syrup, recovery of sucrose from molasses [5,6] in the carbohydrate industry and more recently, the separation of en-

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antiomers [2,7–10] in the biotechnological, pharmaceutical and fine chemistry industries.

Although the SMB technology offers many advantages over preparative chromatography, leading to cleaner, smaller, safer and faster processes [9], the main disadvantage of this process is the limitation to the separation of binary mixtures or to the recovery of one component from a multicomponent mixture.

The process described here is based on the New JO SMB process first applied by the Japan Organo Company (http://www.organo.co.jp/technology/hisepa/en_hisepa/) [11] using patented technology [12,13]. This technique of pseudo-simulated moving bed chromatography is being applied in the separation of complex multicomponent mixtures, e.g. separation of beet molasses mixtures into raffinose, sucrose, glucose and betaine [13] and in the production of raffinose [14] from beet molasses.

In this work, the Pseudo-SMB model of the JO process for the separation of a ternary mixture is developed and the effect of operating conditions (duration of step 1 and step 2, t_{S1} and t_{S2}, respectively) and mass transfer coefficient, k_P on the process performance is addressed.

2. Pseudo-SMB model for the JO process

The JO process used for the separation of ternary mixtures, is also a cyclic process, in which a cycle is constituted by the following two steps:

(1) In the first step, the feed and eluent streams enter the system and the component B with intermediate affinity is recovered; this step is modeled as a series of preparative chromatographic columns.

(2) In the second step, there is only one inlet flow of eluent and no feed; the more retained component C is recovered in the extract and the less adsorbed species A is recovered in the raffinate; this step is modeled as a pseudo true moving bed with no feed. At the end of this step, the intermediate species B is located downstream of the feed point.

The dynamics of the process is explained in detail in Section 4, together with the results obtained for one particular system, denominated by *case study*.

Fig. 1a,b shows the traditional True Moving Bed (TMB) system and the schematic diagram of both step1 and step 2 of the JO process, respectively. The distance coordinate z increases as shown in Fig. 1.

In the traditional TMB system [15], shown in Fig. 1a, there are four sections separated by the inlet and outlet streams; section 1 is between the eluent and extract ports, section 2 between extract and feed ports, section 3 between feed and raffinate ports and section 4 between raffinate and eluent ports and the fluid leaving section 4 is recycled to section 1. Each section contains N_c columns with length L_c.

In the pseudo-SMB model of the JO process, shown in Fig. 1b, we still consider four sections for convenience: (a) in step 1 the feed flows through sections 3 and 4 and the sum of feed plus eluent flow-rates flows through sections 1 and 2; (b) in step 2, equivalent to a TMB model, the flow-rate in sections 2 and 3 is the same since there is no feed.

The detailed mathematical model for the JO process is described below.

2.1. Step 1

This step is modeled as a series of chromatographic columns arranged in four sections. The circuit is cut between sections 2 and 3 by a shut-off valve, allowing an intermediate stream, rich in the intermediate component, to be collected. During step 1, there are two input flows: eluent, Q_{E11}, and feed, Q_F, and one output flow of the intermediate species B, Q_I (Fig. 1b).

The model equations are as follows.

2.1.1. Mass balances for species i in the bulk fluid phase

The mass balance in a volume element of section j is:

$$\frac{\partial c_{ij}}{\partial t} = D_{Lj}\frac{\partial^2 c_{ij}}{\partial z^2} - v_j\frac{\partial c_{ij}}{\partial z} - \frac{(1-\varepsilon)}{\varepsilon}k_P(q_{ij}^{*} - q_{ij}) \qquad (1)$$

where the subscripts i (i=A, B, C) refer to the species in the mixture, and j ($j=1, 2, \ldots, N_S=4$) is the section number, c_{ij} and q_{ij} are the fluid phase and average adsorbed phase concentrations of species i in section j of the preparative column series, respectively, z is the axial co-ordinate, t is the time variable, ε is the bed porosity, v_j is the interstitial fluid velocity in the jth section, D_{Lj} is the axial dispersion coeffi-

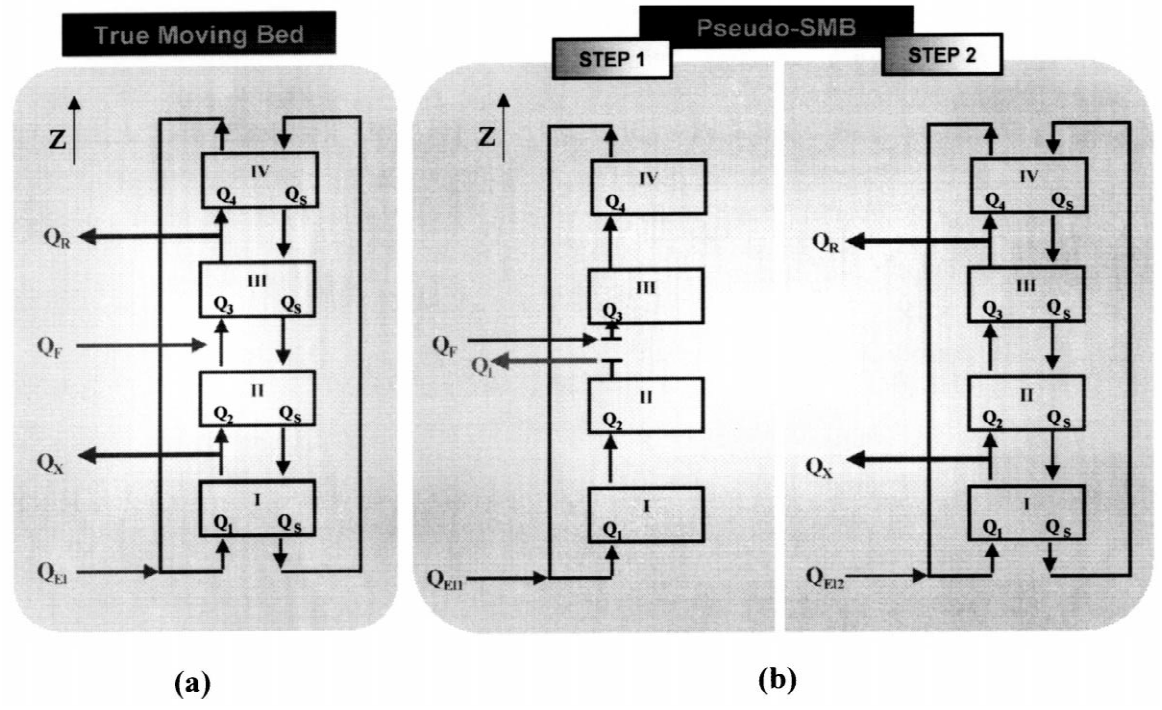

Fig. 1. Comparison between the two different techniques: TMB and (b) Pseudo-SMB JO process.

cient, and k_P is the intraparticle mass transfer coefficient.

2.1.2. Mass balances for species i in the particle

The mass balance in the particle is:

$$\frac{\partial q_{ij}}{\partial t} = k_P(q_{ij}^* - q_{ij}) \tag{2}$$

where q_{ij}^* is the adsorbed phase concentration in equilibrium with c_{ij}.

2.1.3. Initial and boundary conditions

The initial condition for step 1 is:

$$t = 0\ (cycle\ 1)\text{: } c_{ij} = q_{ij} = 0 \tag{3a}$$

$$t = t_{S2}\ (cycle\ k)\text{: } c_{ij} = c_{ij}(cycle\ k-1, step\ 2);$$
$$q_{ij} = q_{ij}(cycle\ k-1, step\ 2) \tag{3b}$$

and the two boundary conditions for section j are given by:

$$z = 0\text{: } c_{ij,0} = c_{ij} - \frac{D_{Lj}}{v_j}\frac{dc_{ij}}{dz} \tag{4a}$$

where $c_{ij,0}$ is the inlet concentration of species i in section j.

$$z = L_j$$

$$\text{Feed node: } c_{i3,0} = c_i^F \tag{4b}$$

$$\text{Eluent node: } c_{i1,0} = \frac{Q_4}{Q_1}c_{i4,1} \tag{4c}$$

Raffinate ($j = 3$) and extract ($j = 1$) nodes:

$$c_{ij,1} = c_{ij+1,0} \tag{4d}$$

Introducing the following dimensionless variables for space and time $x = \frac{z}{L_j}$ and $\theta = \frac{t}{\tau_2}$, respectively, with $\tau_2 = \frac{L_j}{u_s} = N_c t^*$ and $u_s = \frac{L_c}{t^*}$ where t^* is the SMB switch time interval and u_s is the solid velocity in the equivalent true moving bed (TMB), N_c is the

number of columns per section in a SMB unit and L_j is the length of a SMB section, the two mass balances become:

$$\frac{\partial c_{ij}}{\partial \theta} = \gamma_j \left(\frac{1}{\mathrm{Pe}_j} \frac{\partial^2 c_{ij}}{\partial x^2} - \frac{\partial c_{ij}}{\partial x} \right) - \frac{(1-\varepsilon)}{\varepsilon} \alpha_i (q_{ij}^* - q_{ij}) \tag{5}$$

$$\frac{\partial q_{ij}}{\partial \theta} = \alpha_i (q_{ij}^* - q_{ij}) \tag{6}$$

where the model parameters are:

$\mathrm{Pe} = \dfrac{v_j L_j}{D_{\mathrm{L}j}}$, Peclet number

$\alpha_i = \tau_2 k_{\mathrm{P}}$, number of intraparticle mass transfer units

$\gamma_j = \dfrac{\tau_2}{\tau_j} = \dfrac{v_j}{u_{\mathrm{s}}}$,

ratio of fluid and solid interstitial velocities

The initial condition and the boundary conditions for $x=1$ are the same as defined above in Eqs. (4b)–(4d). The boundary condition for $x=0$, in the dimensionless form becomes:

$$c_{ij,0} = c_{ij} - \frac{1}{\mathrm{Pe}_j} \frac{\mathrm{d}c_{ij}}{\mathrm{d}x} \tag{7}$$

2.2. Step 2

This step is modeled as an equivalent TMB with four sections with recycling. During step 2, there is one input flow of eluent, Q_{EI2} and two output flows of extract, Q_{X}, rich in the more retained component C, and raffinate, Q_{R}, rich in the less retained component A. Since there is no feed, the flow-rates in sections 2 and 3 are equal.

Model equations are the species mass balances in the section j of the equivalent true moving bed. In dimensionless form we have:

2.2.1. Bulk fluid phase

$$\frac{\partial c_{ij}}{\partial \theta} = \gamma_j \left[\frac{1}{\mathrm{Pe}_j} \frac{\partial^2 c_{ij}}{\partial x^2} - \frac{\partial c_{ij}}{\partial x} \right] - \frac{(1-\varepsilon)}{\varepsilon} \alpha_j (q_{ij}^* - q_{ij}) \tag{8}$$

2.2.2. Particle

$$\frac{\partial q_{ij}}{\partial \theta} = \frac{\partial c_{ij}}{\partial x} + \alpha_j (q_{ij}^* - q_{ij}) \tag{9}$$

2.2.3. Initial and boundary conditions

The initial condition for this step is:

$\theta = 0$ (cycle 1): $c_{ij} = c_{ij}$(cycle 1, step 1);

$q_{ij} = q_{ij}$(cycle 1, step 1) (10a)

$\theta = \theta_{\mathrm{S1}}$ (cycle k): $c_{ij} = c_{ij}$(cycle k, step 1);

$q_{ij} = q_{ij}$(cycle k, step 1) (10b)

and the two boundary conditions for section j are given by Eqs. (4c), (4d) and (7).

2.3. Numerical solution

The transient Pseudo-SMB model equations are numerically solved, starting from an initial condition where the columns are filled only with the eluent until the cyclic steady-state, CSS, is reached. The CSS is considered to be achieved when:

(i) The relative errors between the average concentrations (evaluated during a full cycle: step 1+ step 2) of each component in the extract, raffinate and intermediate streams for two successive iterations are less than a minimum error defined by the user;

(ii) The relative errors between the total amount of each component that enters in the feed stream and that leaves the system in the extract, raffinate and intermediate streams, evaluated during a full cycle, are less than a minimum error defined by the user.

However, a global error, e_{T}, was used that is defined by:

$$e_{\mathrm{T}} = e_{\mathrm{X}} + e_{\mathrm{R}} + e_{\mathrm{I}} + e_{\mathrm{A}} + e_{\mathrm{B}} + e_{\mathrm{C}} \tag{11}$$

where e_{X}, e_{R} and e_{I} are the relative errors of the average concentrations of the three components ($i=$ A, B, C) in the extract, raffinate and intermediate streams, respectively, for two successive iterations, it and $it-1$, i.e.

$$e_X = \sum_i \frac{|c_{i,X[it]} - c_{i,X[it-1]}|}{c_{i,X[it]}},$$
$$e_R = \sum \frac{|c_{i,R[it]} - c_{i,R[it-1]}|}{c_{i,R[it]}} \text{ and}$$
$$e_I = \sum \frac{|c_{i,I[it]} - c_{i,I[it-1]}|}{c_{i,I[it]}} \quad (12)$$

and e_A, e_B, e_C are the relative error between the amount of species A, B and C, respectively, that enters in the feed stream and leaves the system in the extract, raffinate and intermediate streams, during each cycle, i.e.

$$e_A = \frac{|Q_F c_{A,F} t_{S1} - (Q_X c_{A,X} t_{S2} + Q_R c_{A,R} t_{S2} + Q_I c_{A,I} t_{S1})|}{Q_F c_{A,F} t_{S1}} \quad (13a)$$

$$e_B = \frac{|Q_F c_{B,F} t_{S1} - (Q_X c_{B,X} t_{S2} + Q_R c_{B,R} t_{S2} + Q_I c_{B,I} t_{S1})|}{Q_F c_{B,F} t_{S1}} \quad (13b)$$

$$e_C = \frac{|Q_F c_{C,F} t_{S1} - (Q_X c_{C,X} t_{S2} + Q_R c_{C,R} t_{S2} + Q_I c_{C,I} t_{S1})|}{Q_F c_{C,F} t_{S1}} \quad (13c)$$

The CSS is considered to be achieved when the global error, e_T, is less than a minimum error defined by the user, δ; $\delta = 0.02$ was used in this work.

Model equations were numerically solved using the software package PDECOL [16] based on the method of lines and uses orthogonal collocation in finite elements (OCFE) for the discretization of the space variable. For a ternary system there are six PDEs per section; they are discretized in the axial direction using 20 finite elements and two interior collocation points in each element; the resulting system of ODEs in the time variable is integrated with the solver GEARIB [17].

The parameters used to characterize the CSS performance of a SMB unit are: purity (PU), productivity (PR), recovery (RC) and solvent consumption (SC). In the case of the separation of a ternary mixture using the Pseudo-SMB system, there are three distinct outlet flows, and the following nomenclature will be used: The less retained component (A) is recovered in the raffinate R, the intermediate component (B) is recovered in the intermediate outflow I and the more retained component (C) is recovered in the extract X. The purity and recovery parameters are defined for the three product lines: extract, intermediate and raffinate, while the solvent consumption and productivity parameters are defined in terms of the total amount of solutes recovered (Table 1).

3. Determination of the operating conditions

Once the model for the pseudo-SMB JO system

Table 1
Performance criteria for a pseudo-SMB process

	Extract	Intermediate	Raffinate
Purity (%)	$PUX = 100\frac{C_{C,X}}{C_{A,X} + C_{B,X} + C_{C,X}}$	$PUI = 100\frac{C_{B,I}}{C_{A,I} + C_{B,I} + C_{C,I}}$	$PUR = 100\frac{C_{A,R}}{C_{A,R} + C_{B,R} + C_{C,R}}$
Recovery (%)	$RCX = 100\frac{Q_X C_{C,X} t_{S2}}{Q_F C_{C,F} t_{S1}}$	$RCI = 100\frac{Q_I C_{B,I}}{Q_F C_{B,F}}$	$RCR = 100\frac{Q_R C_{A,R} t_{S2}}{Q_F C_{A,F} t_{S1}}$
Productivity (g/h per l bed)	$PRX = \frac{Q_X C_{C,X}}{V_{SP}} \frac{t_{S2}}{t_{S1} + t_{S2}}$	$PRI = \frac{Q_I C_{B,I}}{V_{SP}} \frac{t_{S1}}{t_{S1} + t_{S2}}$	$PRR = \frac{Q_R C_{A,R}}{V_{SP}} \frac{t_{S2}}{t_{S1} + t_{S2}}$
Solvent consumption (l/g)	$SCX = \frac{Q_{EI1} t_{S1} + Q_{EI2} t_{S2}}{Q_X C_{C,X} t_{S2}}$	$SCI = \frac{Q_{EI1} t_{S1} + Q_{EI2} t_{S2}}{Q_B C_{B,I} t_{S1}}$	$SCR = \frac{Q_{EI1} t_{S1} + Q_{EI2} t_{S2}}{Q_R C_{A,R} t_{S2}}$

has been set, one has to determine the operating conditions, i.e. internal flow-rates in each section and the duration of steps 1 and 2 in order to obtain the desired separation. In this work, a method is suggested based on the definition of velocity of propagation of concentration of a species *i* and on constraints for steps 1 and 2 of the cycle.

The velocity of a propagation of a concentration for component *i* in a fixed bed *j*, is given by [18]:

$$v_{ij} = \frac{v_j}{\left(1 + \frac{1-\varepsilon}{\varepsilon}K_i\right)} = \frac{Q_j}{\varepsilon A\left(1 + \frac{1-\varepsilon}{\varepsilon}K_i\right)} \tag{14a}$$

and the velocity of propagation of a concentration of component *i* in a section *j* of a true moving bed (TMB) is given by:

$$v_{ij} = \frac{v_j - \frac{(1-\varepsilon)}{\varepsilon}u_s K_i}{\left(1 + \frac{1-\varepsilon}{\varepsilon}K_i\right)} = \frac{Q_j - Q_s K_i}{\varepsilon A\left(1 + \frac{1-\varepsilon}{\varepsilon}K_i\right)} \tag{14b}$$

where v_{ij} is the velocity of propagation of a concentration of component *i* in the section *j*, v_j is the interstitial fluid velocity in section *j*, u_s is the interstitial solid velocity and K_i is the slope of the linear adsorption equilibrium isotherm for component *i*.

The distance, x_{ij} traveled by the molecules of species *i*, in step 1 treated as fixed bed (FB) during the time of step 1, t_{S1} is:

$$x_{ij}(\mathrm{FB}) = \frac{t_{S1}Q_j}{\varepsilon A\left(1 + \frac{1-\varepsilon}{\varepsilon}K_i\right)} \tag{15a}$$

and in step 2 treated as true moving bed (TMB), the distance traveled by each component during the time of step 2, t_{S2} is:

$$x_{ij}(\mathrm{TMB}) = \frac{t_{S2}(Q_j - Q_s K_i)}{\varepsilon A\left(1 + \frac{1-\varepsilon}{\varepsilon}K_i\right)} \tag{15b}$$

For a given feed flow-rate, Q_F, and a given t_{S2}, conditions have to be met in order to separate all the three different components.

3.1. Conditions for step 1

The duration of the step 1, t_{S1} is assumed to be the time necessary to feed the intermediate component, B, only in the first column of section 3 on the upstream of the feed. The time, t_{S1}, can be calculated from the pulse response of a fixed bed; if the adsorption isotherm of this component is linear, the transfer function, $G(s)$ is:

$$G(s) = \exp\left(\frac{\mathrm{Pe}}{2}\left\{1 - \sqrt{4\frac{\tau}{\mathrm{Pe}}\left[1 + \frac{(1-\varepsilon)}{\varepsilon}\frac{k_P K_B}{s + k_P}\right]s}\right\}\right) \tag{16}$$

The retention time of the species B is the first moment of the pulse response [19], i.e.

$$\bar{t}_B = \tau\left[1 + \frac{(1-\varepsilon)}{\varepsilon}K_B\right] \tag{17}$$

where $\tau = \frac{\varepsilon A L_c}{Q_F}$ and the variance $\sigma^2 = \mu_2 - \mu_1^2$ of the pulse response is:

$$\sigma^2 = \frac{2}{\mathrm{Pe}}\left[1 + \frac{(1-\varepsilon)}{\varepsilon}K_B\right]^2\tau^2 + \frac{2}{k_P}\frac{(1-\varepsilon)}{\varepsilon}K_B\tau \tag{18}$$

Finally, the standard deviation is:

$$\sigma = \sqrt{\frac{2\bar{t}_B^2}{\mathrm{Pe}} + \frac{2}{k_P}(\bar{t}_B - \tau)} \tag{19}$$

In order to guarantee that no component B is present in the second column of section 3, within an assumed error of less than 5%, the duration of step 1 is given by:

$$t_{S1} = \bar{t}_B - 2\sigma = \bar{t}_B - 2\sqrt{\frac{2\bar{t}_B^2}{\mathrm{Pe}} + \frac{2}{k_P}(\bar{t}_B - \tau)} \tag{20a}$$

In the case of $\mathrm{Pe} \gg 1$, the above equation becomes:

$$t_{S1} = \bar{t}_B - \sqrt{\frac{8}{k_P}}\sqrt{(\bar{t}_B - \tau)} \tag{20b}$$

In the cyclic steady-state, the step 1 follows a step 2 and in order to collect the intermediate species B just before the feed node, the eluent flow-rate, Q_{El1},

is such that component B travels with the liquid, in section 2, a distance equal to $2L_c$, i.e.

$$Q_{EI1} = \frac{\varepsilon A(2L_c)}{t_{S1}}\left(1 + \frac{1-\varepsilon}{\varepsilon}K_B\right) - Q_F \quad (21)$$

For outlet flow with the intermediate component B, is $Q_I = Q_{FE} + Q_{EI1}$. The operating conditions for the step 1 are then given by Eqs. (20b) and (21).

3.2. Conditions for step 2

The determination of the internal flow-rates for step 2, are based on the following assumptions:

- Component B (intermediate species) moves $(x_{B,S1} + 1.5L_c)$ with the solid in order to stay totally downstream of the feed point in section 2;
- Component C (more retained species) moves $(x_{C,S1} + 3.5L_c)$ with the solid in order to stay centered in the extract.

The first two assumptions lead to the following equations:

$$x_{B,S2} = -(x_{B,S1} + L_c) = \frac{t_{S2}}{\varepsilon A\left(1 + \frac{1-\varepsilon}{\varepsilon}K_B\right)}(Q_{3,S2} - Q_S K_B) \quad (22)$$

$$x_{C,S2} = -(x_{C,S1} + 3L_c) = \frac{t_{S2}}{\varepsilon A\left(1 + \frac{1-\varepsilon}{\varepsilon}K_C\right)}(Q_{3,S2} - Q_S K_C) \quad (23)$$

Furthermore some constraints have to be met in order to: (a) recover A in the raffinate and guarantee that A is not recycled to section 1 with the liquid and (b) recover C in the extract and guarantee that no C is carried with the solid to section 4. These constraints are expressed in terms of net fluxes of components C and A in sections 1 and 4, respectively, i.e.

$$\frac{Q_{1,S2} + \frac{t_{S1}}{t_{S2}}(Q_F + Q_{EI1})}{Q_S K_C} > 1 = \beta \quad (24)$$

$$\frac{Q_{4,S2} + \frac{t_{S1}}{t_{S2}}Q_F}{Q_S K_A} < 1 = \frac{1}{\beta} \quad (25)$$

where the safety margin, β, is $\beta > 1$. These constraints take into account the correction of the liquid flow-rates due to the displacement of the internal concentration profiles during step 1.

Solving Eqs. (22) and (23) relative to Q_3 and Q_S, we obtain:

$$Q_{3,S2} = \frac{\varepsilon A}{t_{S2}}\left\{\frac{K_B}{K_B - K_C}\left[x_{C,S2}\left(1 + \frac{1-\varepsilon}{\varepsilon}K_C\right) - x_{B,S2}\left(1 + \frac{1-\varepsilon}{\varepsilon}K_B\right)\right] + x_{B,S2}\left(1 + \frac{1-\varepsilon}{\varepsilon}K_B\right)\right\} \quad (26)$$

$$Q_S = \frac{\varepsilon A}{t_{S2}}\left\{\frac{1}{K_B - K_C}\left[x_{C,S2}\left(1 + \frac{1-\varepsilon}{\varepsilon}K_C\right) - x_{B,S2}\left(1 + \frac{1-\varepsilon}{\varepsilon}K_B\right)\right]\right\} \quad (27)$$

The equations for the liquid flow-rates in the various sections are then given by:

$$Q_{2,S2} = Q_{3,S2}$$

$$Q_{1,S2} = Q_S K_C \beta - (Q_{FE} + Q_{EI1})\frac{t_{S1}}{t_{S2}} \quad (28)$$

$$Q_{4,S2} = \frac{Q_S K_A}{\beta} - Q_{FE}\frac{t_{S1}}{t_{S2}} \quad (29)$$

Now all internal flow-rates for step 2 treated as a TMB are defined. The input flow of eluent, Q_{EI2}, and output flows of raffinate, Q_R, and extract, Q_X are:

$$Q_R = Q_{3,S2} - Q_{4,S2} \quad (30)$$

$$Q_X = Q_{1,S2} - Q_{2,S2} \quad (31)$$

$$Q_{EI2} = Q_{1,S2} - Q_{4,S2} \quad (32)$$

4. Case study

4.1. Parameters

The pseudo-SMB model for the JO process was tested using the ternary system shown in Table 2. The characteristics of the physical system (Japan Organo Catalog, 1998) are shown in Table 3. It is assumed that the mass transfer coefficient, $k_p = 0.5$

Table 2
Adsorption parameters and concentrations for the ternary mixture (case study)

Component	Linear isotherm parameter (K_i)	C_0 (g/l)
A (less retained)	0.19	100
B (intermediate)	0.39	100
C (more retained)	0.65	100

Table 3
Characteristics of the SMB columns

Column number (total)	12
Column length (cm)	120
Column diameter (cm)	10.84
Column volume (l)	11.1
Number of columns per section	3
Bed porosity (ε)	0.4

s^{-1} and the Peclet number, Pe = 2000. For the case study, the feed flow-rate and the duration of step 2 are: $Q_F = 350$ ml/min and $t_{S2} = 66$ min (Organo Catalog, 1998). The duration of step 1 according to Eq. (20a) is $t_{S1} = 18.17$ min. The global error, $e_T <$ 2% and a safety margin step, $\beta = 1.03$ were fixed. The parameters of the model are shown in Table 4, and in Fig. 2.

4.2. Results

Fig. 3 shows the concentration profiles in the liquid phase at the end of step 1 and step 2, for cycles 1, 2 and 20, the latter obtained after cyclic steady state, CSS, was achieved.

The feed containing solutes A, B and C with species concentration $C_0 = 100$ g/l is injected in step 1 of the cycle during $0 < t \leq t_{S1}$ with flow-rate Q_F, at the inlet of section 3. At the same time, there is an intermediate stream, Q_I, coming out from the end of section 2, although in the first cycle this intermediate stream only contains the eluent.

During the second step of the cycle for $t_{S1} < t \leq t_{S2}$, the feed flow and the flow of intermediate species are stopped; there are two outlet streams: one at the end of section 1 — Extract, Q_X, and the other at the end of section 2 — Raffinate, Q_R. At the same time, it is assumed that the solid starts moving in the opposite direction to the fluid. The component A moves in the direction of the fluid but components B and C move in the opposite direction, i.e. in the direction of the solid phase.

However, at the end of cycle 1, component C has already reached the end of section 1 and is also coming out in the extract stream, component B is well separated from C and completely inside section 2 and finally, component A did not reach the end of section 3 and so it is not as yet coming out in the raffinate. It should be noted that at the end of this first cycle, all the A and B components injected in the first step were accumulated inside the system, as well as part of the C component.

As described above for cycle 1, during the first step of cycle 2, $t_{S2} < t \leq [t_{S1} + (t_{S1} + t_{S2})]$, there is a feed stream injecting more A, B and C mixture in the beginning of section 3 and an intermediate stream leaving at the end of section 2. Fig. 3 shows that at the end of step 1 of cycle 2, all the B component was collected in the intermediate stream, while the other components that were accumulated in the last cycle just moved with the fluid. It can be seen that, during this step, component A reached the end of section 3.

Table 4
Model parameters

Parameter	Step 1	Step 2
Step time, $t_{S1,2}$ (min)	18.17	66.0
Solid residence time (in step 2), τ_2 (min)	–	17.0
Peclet number	2000	2000
Number of mass transfer units, $\alpha_i = \tau_2 k_P$ ($k_P = 0.5$ s^{-1})	510.8	510.8
Ratio between fluid and solid velocities	–	$\gamma_1 = 0.73$
	–	$\gamma_2 = 0.38$
	–	$\gamma_3 = 0.38$
	–	$\gamma_4 = 0.15$
Solid/fluid volumes $(1 - \varepsilon)/\varepsilon$	1.5	

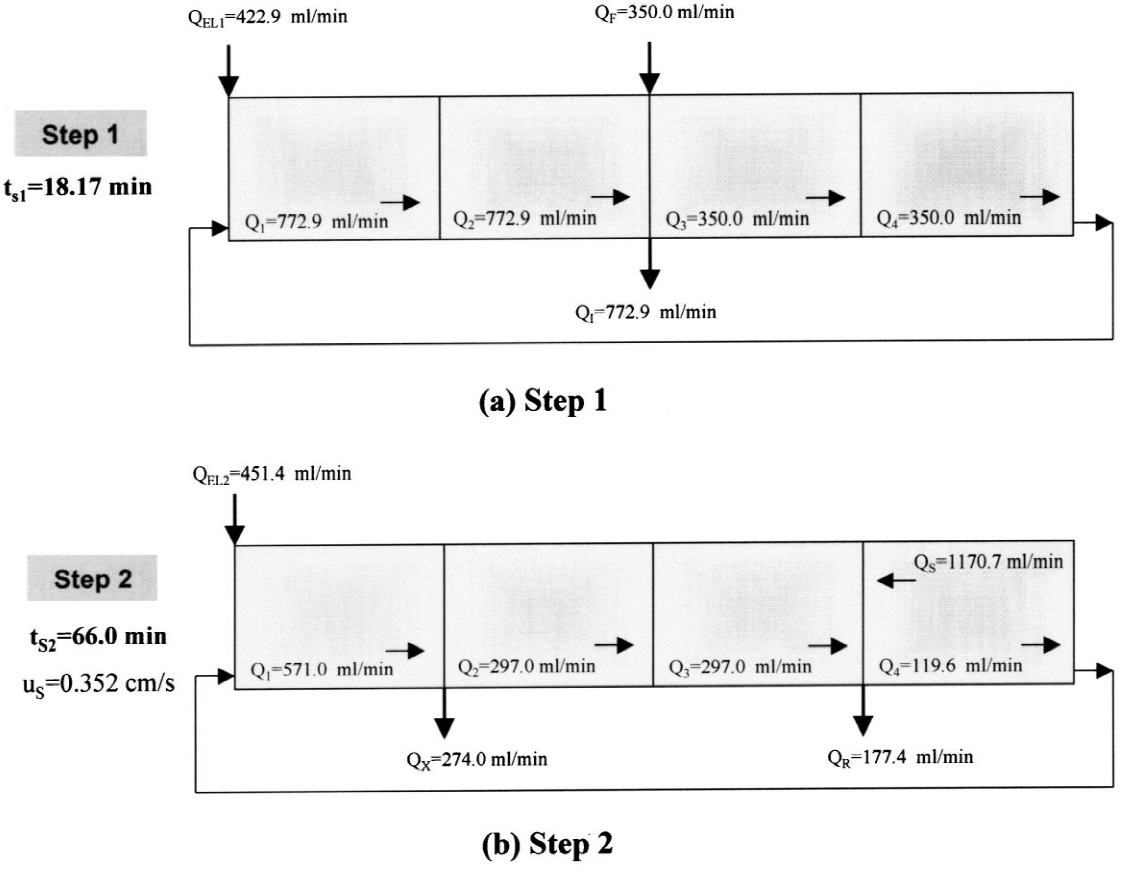

Fig. 2. Schematic diagram showing the variables used in (a) step 1 and (b) step 2, for the case study.

Then the step 2 of cycle 2, during $[t_{S1}+(t_{S1}+t_{S2})]<t\leq t_{S2}$ follows. Again, component A moves in the direction of the fluid and component B and C move in the opposite direction. It can be seen that species C injected in cycle 2 merges with the concentration profile of C accumulated during cycle 1; the same happens with component A. Part of these species C and A will leave as extract and raffinate, respectively. At the end of cycle 2 the amount of B is equal to the amount of B at the end of cycle 1, so all the B component is recovered during step 1 of the next cycle. This is important otherwise there will be significant accumulation of B component, until a point that it will contaminate the extract and/or the raffinate streams.

Finally, Fig. 3 shows the concentration profiles for cycle 20, after CSS has been reached ($e_T<2\%$). The behavior is similar to that described for cycle 2, but during step 2 of cycle 20, the amounts of C and A collected in the extract and raffinate are constant.

The movement of the three species is illustrated in Fig. 4 showing concentration profiles at 10, 50 and 100% of t_{S1} and t_{S2}, respectively, for cycle 20, after CSS is achieved.

Fig. 5 shows the evolution of the A, B and C internal concentration profiles at the end of (a) step 1 and (b) step 2, until CSS is reached. It can be seen that there is no B component at the end of step 1, the profile of the B component at the end of step 2 is always the same, and that the other two components reach the CSS in a small number of cycles. During the evolution to the CSS, the only changes are in the left tail of the C component profile and on the right tail of the A component profile.

The species concentrations in the output flows: (a) raffinate, (b) intermediate and (c) extract, are shown

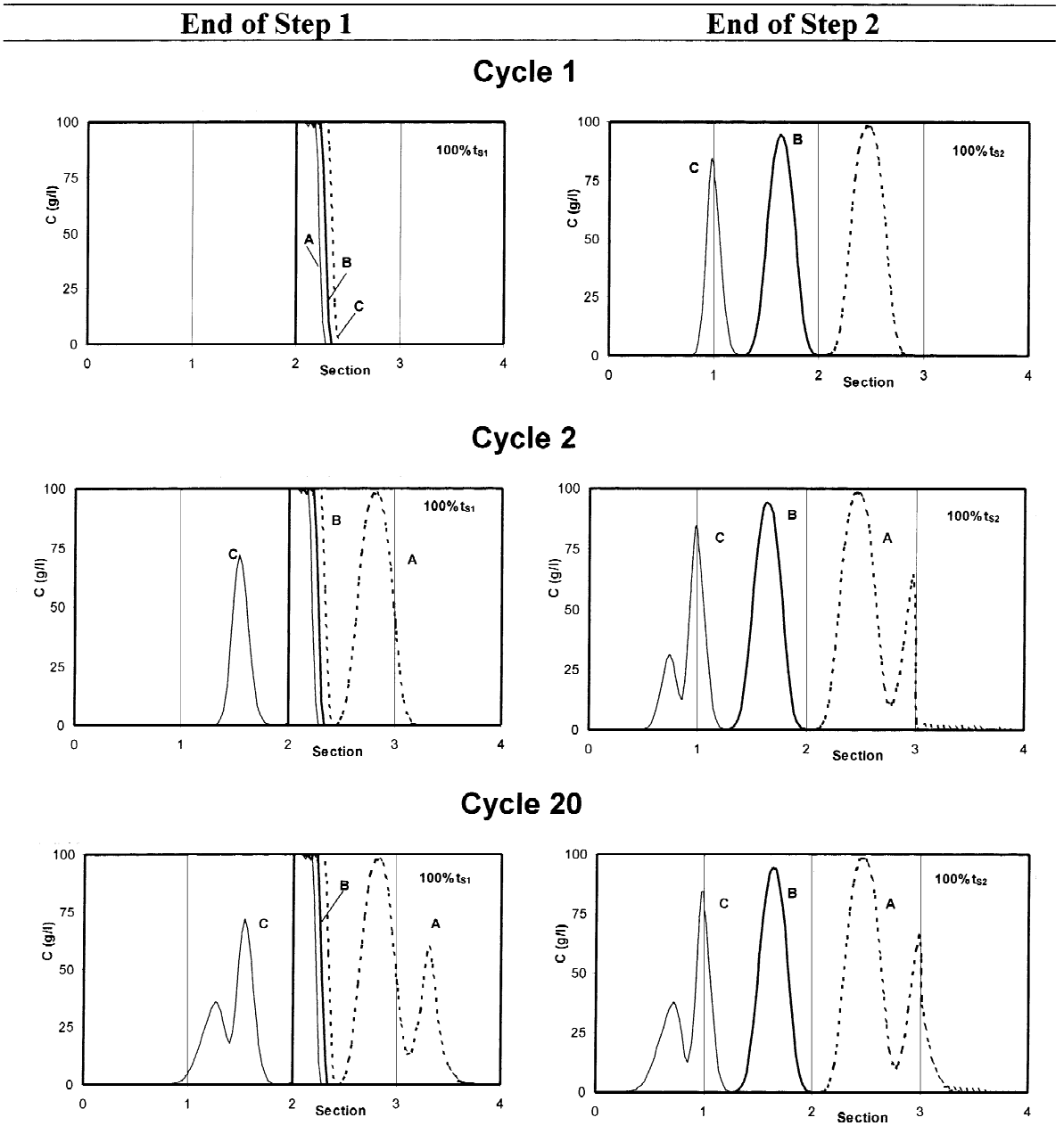

Fig. 3. Concentration profiles, in cycles 1, 2 and 20, at the end of step 1 (left) and at the end of step 2 (right), for the case study.

in Fig. 6, for the first 10 cycles. All the streams have almost only one component in all cycles. After CSS has been reached, these output flows have average concentrations equal to: $\bar{C}_A^R = 52.1$ g/l, $\bar{C}_B^I = 45.3$ g/l and $\bar{C}_C^X = 36.7$ g/l.

The cumulative mass balance, representing the cumulative mass entered in the system (In), the cumulative mass which left the system (Out) and the mass remaining inside the system (Ac) of components A, B and C is shown in Fig. 7, for the first 10 cycles. It can be seen that the cyclic steady state is reached in a small number of cycles.

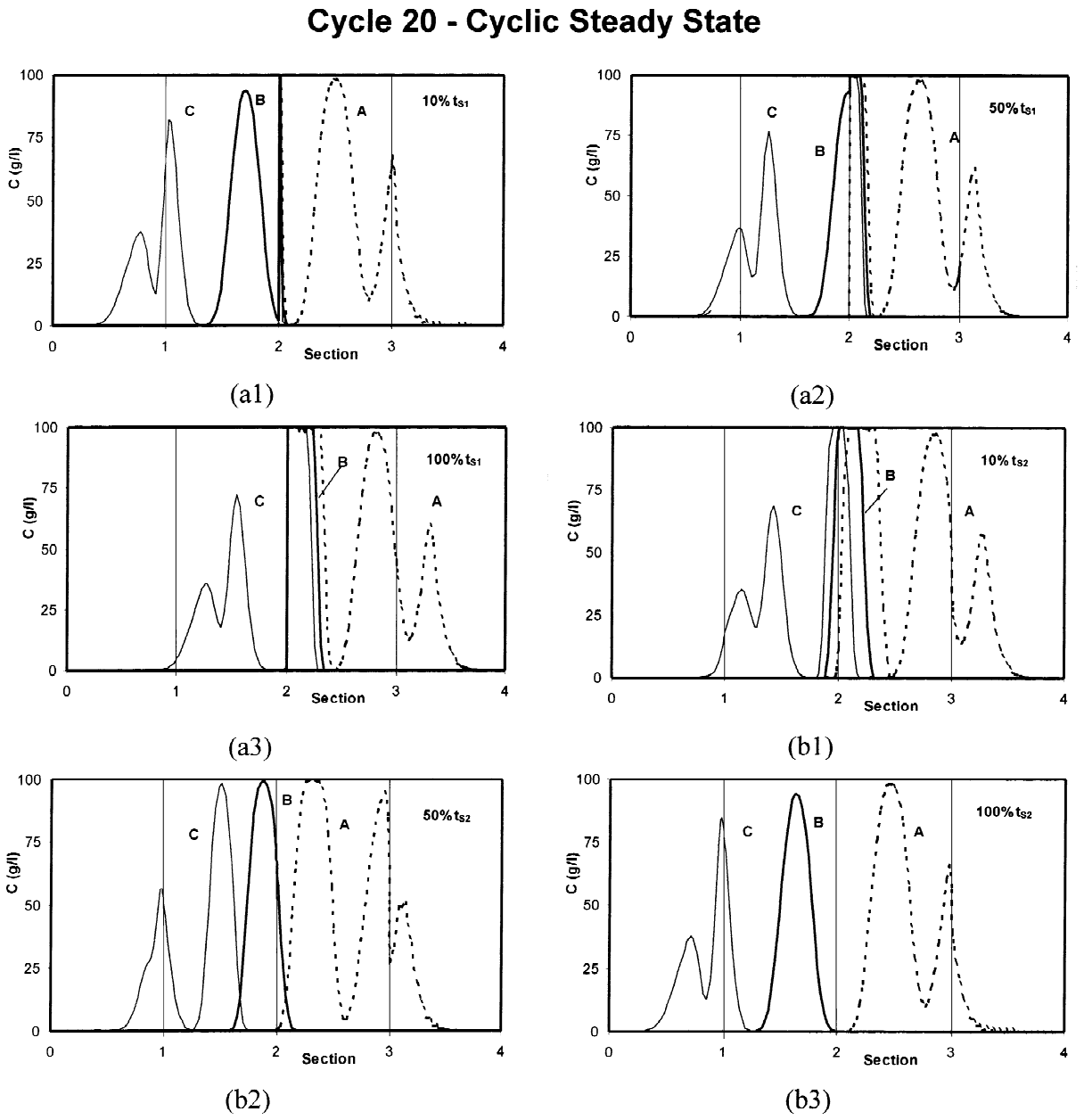

Fig. 4. Evolution of profiles, during step 1 and step 2, in cycle 20 (cyclic steady-state), for the case study.

The process performance indices: (a) Purity, (b) Recovery, (c) Productivity and (d) Solvent consumption in CSS are given in Table 5. The purity and recovery are high for all three components.

The performance of the JO process for the ternary separation reported in the case study was compared with that of two SMBs in series. The comparison was based on the following assumptions:

(a) The constant feed flow-rate of the first SMB was considered to be equal to $Q_{FE}\frac{t_{S1}}{t_{S1}+t_{S2}}$; in fact in the JO system there is only a feed flow-rate Q_{FE}

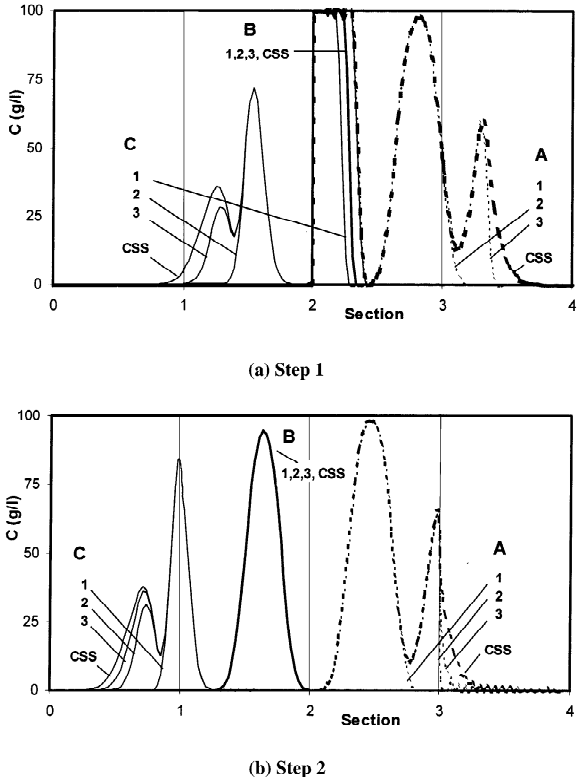

Fig. 5. Profiles obtained at the end of (a) step 1 and (b) step 2, in cycles 1, 2, 3 and 20, for the case study.

during the time of the first step, t_{S1} although the cycle time is $t_{S1} + t_{S2}$.

(b) The inventory of adsorbent in the JO system was equally divided by the two SMBs in series.

The first simulated moving bed, SMB1, uses a feed flow-rate of 75.6 ml/min and is constituted by a solution of A, B and C at a concentration of 100 g/l each. The outlet streams of SMB1 are a raffinate rich in A and an extract which is mainly a mixture of B and C. The second simulated moving bed, SMB2 uses the SMB1 extract (B+C) as the feed stream; the outlet streams of SMB2 are a raffinate rich in B and an extract rich in C.

Table 6 shows the operating conditions (flow-rates of inlet, outlet and recycle streams and switching time) and the outlet concentrations for the SMB1 and in SMB2 in cyclic steady state. Table 7 shows the results of purity, recovery, productivity and solvent consumption obtained after CSS is achieved, for the ternary separation using the two SMBs in series.

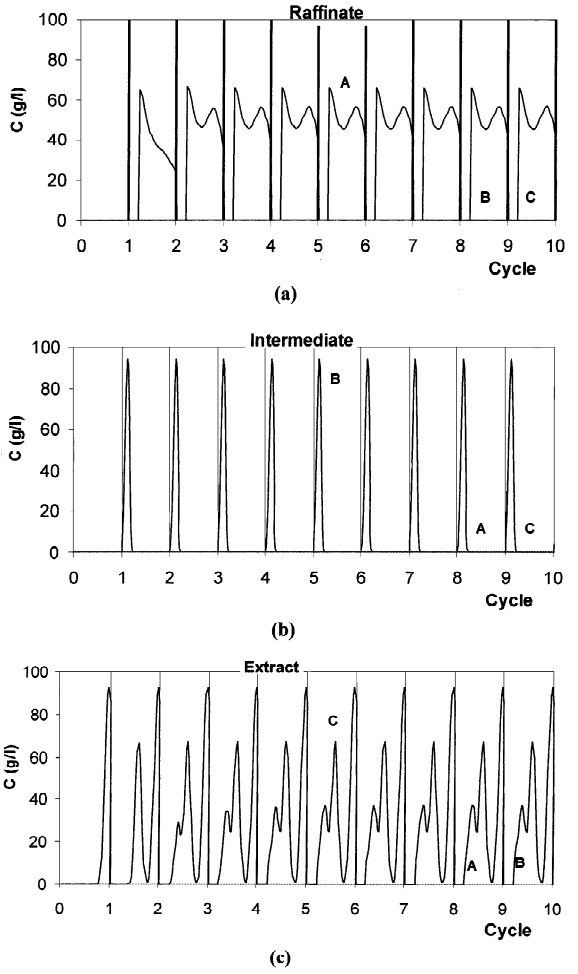

Fig. 6. Evolution of species concentrations in the (a) extract, (b) intermediate and (c) raffinate streams, during 10 cycles.

Comparing these values with those obtained with the JO system (Table 5), it can be seen that purity, recovery, productivity and solvent consumption are similar in both systems. However, the investment in two SMBs is higher than in one JO system.

5. Parameter sensitivity

The influence of the operating conditions t_{S1} and t_{S2}, and intraparticle mass transfer coefficient k_p, was studied. All the internal flow-rates, input and output flow-rates and parameters are those of the case study (Fig. 2).

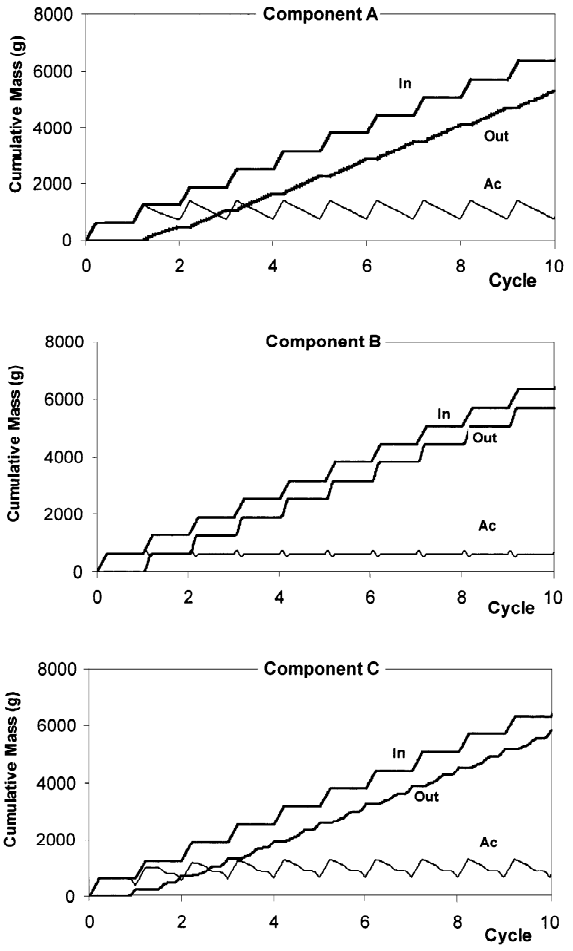

Fig. 7. Evolution of the cumulative mass for component A, B and C, in the first 10 cycles. In, mass which entered the system; Out, mass which left the system; Ac, mass staying inside the system.

Table 6
Operating conditions and outlet concentrations for the two SMBs in series

	SMB1	SMB2
Feed	$Q_{FE}=75.6$ ml/min $c_{A,0}=100$ g/l $c_{B,0}=100$ g/l $c_{C,0}=100$ g/l	$Q_{FE}=195.7$ ml/min $c_B=39.1$ g/l $c_C=39.0$ g/l
Raffinate	$Q_{RA}=80.2$ ml/min $c_A=92.8$ g/l	$Q_{RA}=215.3$ ml/min $c_B=34.7$ g/l
Extract	$Q_{EX}=195.7$ ml/min $c_B=39.1$ g/l $c_C=39.0$ g/l	$Q_{EX}=228.5$ ml/min $c_C=33.0$ g/l
Eluent	$Q_{EL}=200.3$ ml/min	$Q_{EL}=248.1$ ml/min
Recycling flow-rate	$Q_{RC}=351.5$ ml/min	$Q_{RC}=891.8$ ml/min
Switching time	$t^*=8.0$ min	$t^*=3.9$ min

5.1. Influence of the mass transfer coefficient

The mass transfer coefficient, k_P, affects the dispersion of an adsorbed component. Fig. 8 shows the internal concentration profiles for $k_P=0.1\ s^{-1}$. At the end of step 1 (Fig. 8a), it can be seen that not all the intermediate B component was removed from the system during step 1. The left tail of the B front is crossing the right tail of the C front. On the other hand, component A is very close to the end of section 4, and a minor fraction of A is recycled to section 1, contaminating component C. From Fig. 8b, representing the end of step 2, we see that component B is not completely separated from A and C; the left tail of B is contaminating the extract stream and the right tail of B is contaminated with the left tail of A.

The influence of the mass transfer coefficient on the purity of each component in each output flow is shown in Fig. 9. The purity of B in the intermediate

Table 5
Performance criteria of the JO process obtained after CSS, for the case study

	A in Raffinate (during Step 2)	B in Intermediate (during Step 1)	C in Extract (during Step 2)
Purity (%)	100.0	99.98	99.94
Recovery (%)	96.7	99.9	100.0
Productivity (g/day per l bed)	5.49	5.69	5.92
Solvent consumption (l/g)	0.060	0.059	0.056

Table 7
Performance criteria obtained after CSS, for the two SMBs in series

	A in Raffinate 1	B in Raffinate 2	C in Extract 2
Purity (%)	100.0	99.8	99.9
Recovery (%)	98.5	98.9	99.8
Productivity (g/l of adsorbent per h)	5.60	5.62	5.67
Solvent consumption (l/g)	0.06	0.06	0.06

stream is the more affected by a decrease in k_P. It can be concluded that for systems where the components have smaller values of k_P, one has to find the internal flow-rates to optimize the ternary separation.

5.2. Influence of the Step 1 and Step 2 duration

Contrary to the values of k_P that are fixed for each solute–solid system, the values of the time of step 1, t_{S1}, and of step 2, t_{S2}, are two important parameters in the optimization of the Pseudo-SMB system.

To study the influence of t_{S1} on the process performance several values were tested, keeping constant all the other parameters used for the case study, namely, the value of t_{S2}. The t_{S1} values tested were in the range 0.5 t_{S1}–1.5 t_{S1}.

Fig. 10 shows the influence of t_{S1} in the CSS of the Pseudo-SMB system, at the end of step 1 and step 2, for the extreme cases: 0.5 t_{S1} and 1.5 t_{S1} and for the CS.

From Fig. 10a, it can be seen that for smaller values of t_{S1} compared with the CS the species B is not completely removed during step 1; this leads to the contamination of the extract stream by the B component.

For higher values of t_{S1} (Fig. 10c) compared with CS, although component B is completely removed from the system during step 1, part of the C component is also removed in the intermediate stream. During this step, component A is recycled to the section 1, consequently contaminating the extract stream, in step 2.

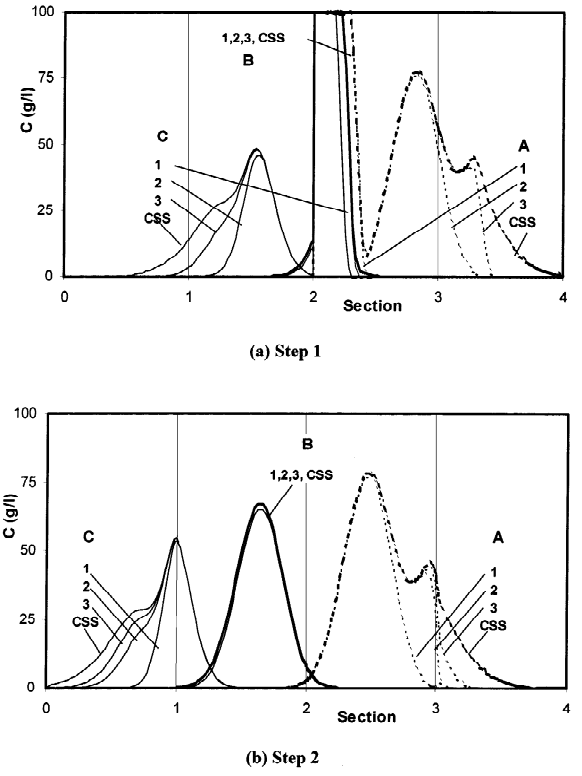

Fig. 8. Profiles obtained at the end of (a) step 1 and (b) step 2, in cycles 1, 2, 3 and 20, for $k_P = 0.1$.

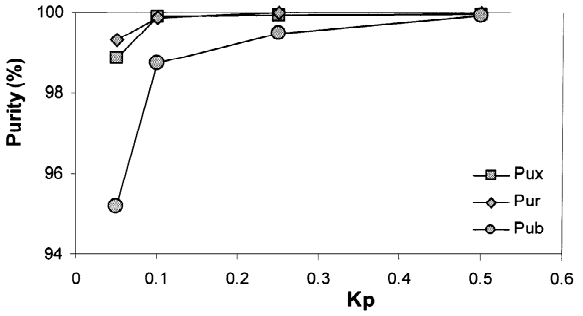

Fig. 9. Effect of k_P on the purity, after 20 cycles.

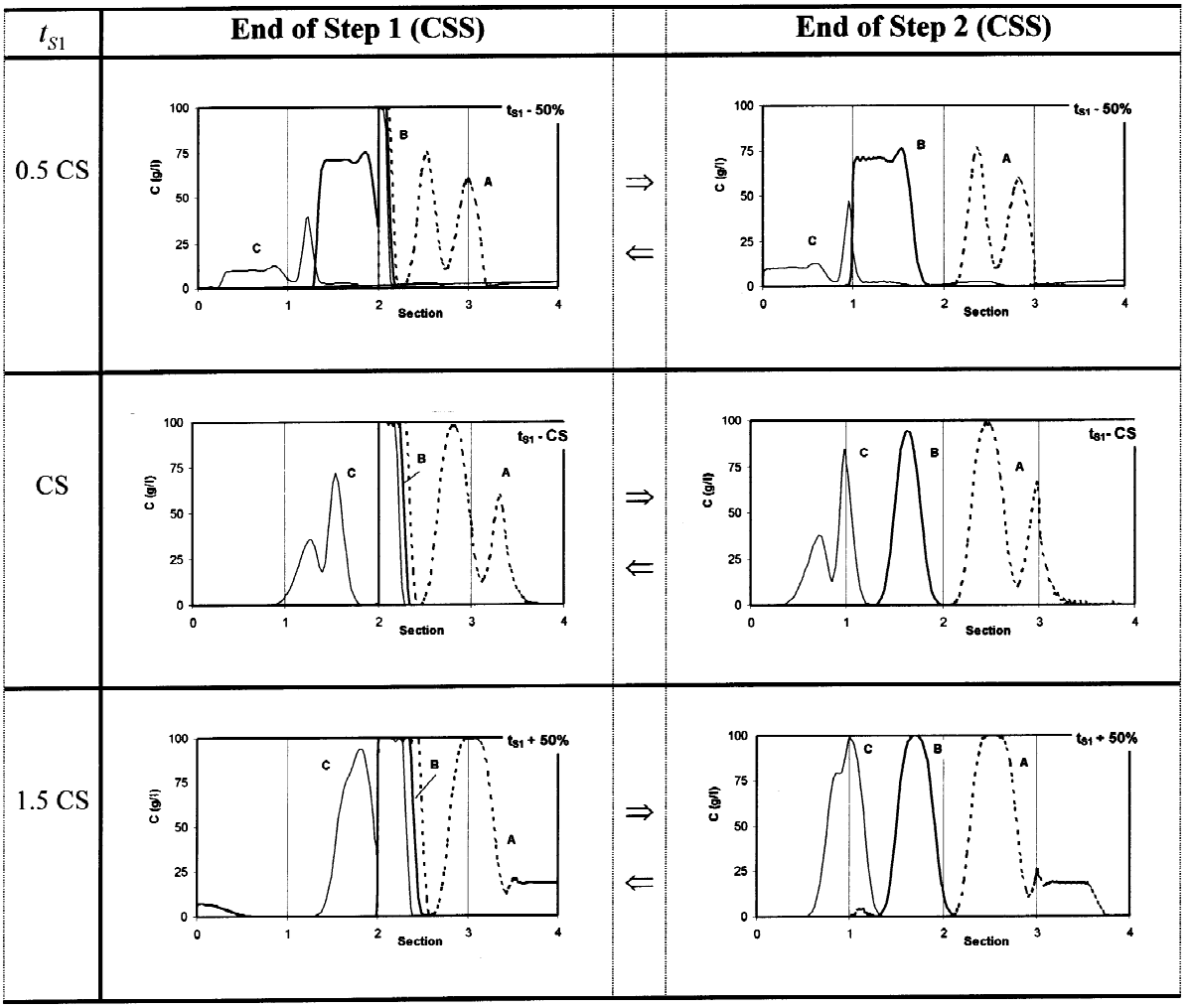

Fig. 10. Effect of t_{S1} on the internal concentration profiles at the end of (i) step 1 and (ii) step 2, after 20 cycles, for t_{S1} equal to (a) 0.5 CS, (b) CS and (c) 1.5 CS.

The effect of t_{S2} was tested by changing its value in the range 0.5 t_{S2}–1.5 t_{S2}. Fig. 11 shows that the effect of smaller values of t_{S2} is identical to the effect of higher values of t_{S1} and that the effect of higher values of t_{S2} is identical to the effect of smaller values of t_{S1}.

The effect of t_{S1} and t_{S2} on the purity of the output streams (Fig. 12) is more pronounced on the concentration of B in the intermediate stream and on the concentration of C in the extract stream.

The effect of t_{S1} and t_{S2} on the recovery is shown in Fig. 13. Recovery decreases for lower values of both t_{S1} and t_{S2}. Higher values of t_{S1} do not have a pronounced effect on the recovery of the three output streams.

6. Conclusions

A model of the JO process for the separation of ternary mixtures by Pseudo-SMB chromatography is described. It considers step 1 of the cycle as a series of preparative chromatographic columns and step 2 as a true moving bed without feed. Operating

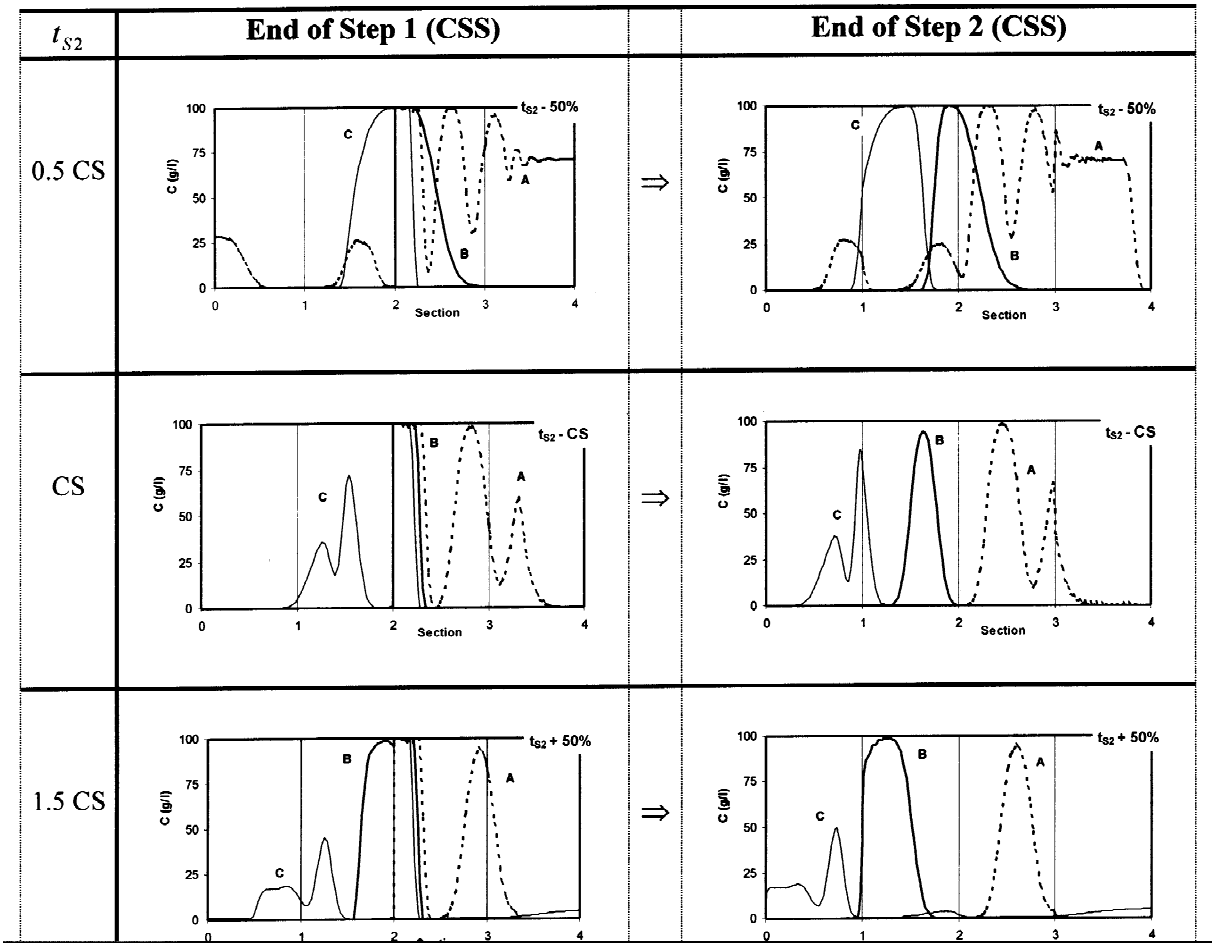

Fig. 11. Effect of t_{S2} on the internal concentration profiles at the end of (i) step 1 and (ii) step 2, after 20 cycles, for t_{S2} equal to (a) 0.5 CS, (b) CS and (c) 1.5 CS.

conditions for both steps of the cycle were suggested based on considerations of velocity of propagation of concentrations of species and constraints of the system. With those conditions all internal flow-rates were calculated. The effect of operating conditions (duration of steps 1 and 2) and mass transfer coefficient on the process performance was analyzed.

7. Nomenclature

A	cross-section area of a column, cm^2
c	fluid phase concentration, g/l
D_L	axial dispersion coefficient, cm^2/s
e_T	global error, %
K_i	linear adsorption isotherm parameter
k_P	mass transfer coefficient, s^{-1}
L_c	column length (cm)
L_j	section length (cm)
Pe	Peclet number
PR	productivity, g/h per l bed
PU	purity, %
q	average adsorbed phase concentration, $g/l_{particle}$

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